

Water Bath Calorimetry on a Catalytic Reaction of Atomic Hydrogen

R. L. Mills*, H. Zea, J. He, B. Dhandapani

BlackLight Power, Inc.

493 Old Trenton Road

Cranbury, NJ 08512

ABSTRACT

Plasmas of certain catalysts such as Sr^+ and Ar^+ mixed with hydrogen were studied for evidence of a novel energetic reaction. These hydrogen plasmas called resonant transfer- or rt-plasmas were observed to form at low temperatures (e.g. $\approx 10^3 K$) and extraordinary low field strengths of about 1-2 V/cm when argon and strontium were present with atomic hydrogen. Time-dependent line broadening of the H Balmer α line was observed corresponding to extraordinarily fast H (25 eV). When an argon-hydrogen hollow-anode glow discharge plasma with strontium metal contained in the cell was optimized for Sr^+ emission, an average hydrogen hot atom temperature of 50.2 eV with a 83.5% population and an excess power of 28.5% of the input power were observed. Using water bath calorimetry, an excess power of 2.85 W was measured on rt-plasmas with Sr^+ and Ar^+ as catalysts and atomic hydrogen as a reactant, compared with controls with no hydrogen and no catalyst present. The energy balance was high. Given an argon-hydrogen (95/5 %) flow rate of 1.0 sccm and an average excess power of 2.85 W and energy balances of over $-7.7 \times 10^4 kJ/mole H_2$ were measured.

Keywords: catalysis, rt-plasma, fast H, excess power

* To whom correspondence should be addressed. Phone: 609-490-1090; Fax: 609-490-1066;
E-mail: rmills@blacklightpower.com

1. Introduction

A new chemically generated or assisted plasma source has been developed that is based on a resonant energy transfer mechanism (rt-plasma). One such source operates by incandescently heating a hydrogen dissociator and a catalyst to provide atomic hydrogen and gaseous catalyst, respectively, such that the catalyst reacts with the atomic hydrogen to produce a plasma. It was extraordinary that intense EUV emission was observed by Mills, et al. [1-4] at low temperatures (e.g. $\approx 10^3$ K) and an extraordinary low field strength of about 1-2 V/cm from atomic hydrogen and certain atomized elements or certain gaseous ions, which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV. A number of independent experimental observations [1-26] confirm that the rt-plasma is due to a novel reaction of atomic hydrogen which produces as chemical intermediates, hydrogen atoms in fractional quantum states that are at lower energies than the traditional "ground" ($n=1$) state. Power is released, and the final reaction products are novel hydride compounds. The supporting data include EUV spectroscopy [1-7, 10, 14-20, 23], characteristic emission from catalysts and the hydride ion products [1-4, 14, 16-20], lower-energy hydrogen emission [5-7, 23], chemically formed plasmas [1-4, 14-20], Balmer α line broadening [1-6, 8-14, 16, 19-20, 23], population inversion of H lines [19-21], elevated electron temperature [6, 8-9], anomalous plasma afterglow duration [14-15], power generation [6, 10, 14, 22-23], and analysis of novel chemical compounds [14, 24-26].

The theory given previously [27-29] is based on applying Maxwell's equations to the wave equation. The familiar Rydberg equation (Eq. (1)) arises for the hydrogen excited states for $n > 1$ of Eq. (2).

$$E_n = -\frac{e^2}{n^2 8\pi\epsilon_0 a_H} = -\frac{13.598 \text{ eV}}{n^2} \quad (1)$$

$$n = 1, 2, 3, \dots \quad (2)$$

An additional result is that atomic hydrogen may undergo a catalytic reaction with certain atoms and ions, which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, $m \cdot 27.2 \text{ eV}$, wherein m is an integer. The reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen that corresponds to a fractional principal quantum number. That is

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots, \frac{1}{p}; \quad p \text{ is an integer} \quad (3)$$

replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states. The $n=1$ state of hydrogen and the $n = \frac{1}{\text{integer}}$ states of hydrogen are nonradiative, but a transition between two nonradiative states, say $n=1$ to $n=1/2$, is possible via a

nonradiative energy transfer. Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2 \text{ eV}$ (i.e. it resonantly accepts the nonradiative energy transfer from hydrogen atoms and releases the energy to the surroundings to affect electronic transitions to fractional quantum energy levels). As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy as $q \cdot 13.6 \text{ eV}$ emission [5-7] or $q \cdot 13.6 \text{ eV}$ transfer to H to form extraordinarily hot, excited-state H [8-13] until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (1) and (3). Processes such as hydrogen molecular bond formation that occur without photons and that require collisions are common [30]. Also, some commercial phosphors are based on resonant nonradiative energy transfer involving multipole coupling [31].

Certain atoms, excimers, and ions which provide a reaction with a net enthalpy of an integer multiple of the potential energy of atomic hydrogen, $E_h = 27.2 \text{ eV}$ where E_h is one hartree. Specific species (e.g. He^+ , Ar^+ , K , and Sr^+) identifiable on the basis of their known electron energy levels are required to be present in plasmas with atomic hydrogen to catalyze the process. In contrast, species such as atoms or ions of Mg or Xe do not fulfill the catalyst criterion—a chemical or physical process with an enthalpy change equal to an integer multiple of E_h that is sufficiently reactive with atomic hydrogen under reaction conditions.

Ar^+ may serve as a catalyst since its ionization energy is about 27.2 eV . Also, since the ionization energy of Sr^+ to Sr^{3+} has a net enthalpy of reaction of $2 \cdot 27.2 \text{ eV}$, Sr^+ may serve as catalyst alone or with Ar^+ catalyst. It was reported previously that an rt-plasma formed with a low field (1 V/cm), at low temperatures (e.g. $\approx 10^3 \text{ K}$), from atomic hydrogen generated at a tungsten filament and strontium which was vaporized by heating the metal [1-4]. Strong VUV emission was observed that increased with the addition of argon, but not when sodium, magnesium, or barium replaced strontium or with hydrogen, argon, or strontium alone. Characteristic emission was observed from a continuum state of Ar^{2+} at 45.6 nm without the typical Rydberg series of Ar I and Ar II lines which confirmed the resonant nonradiative energy transfer of 27.2 eV from atomic hydrogen to Ar^+ [2, 4, 18]. Predicted Sr^{3+} emission lines were also observed from strontium-hydrogen plasmas [2, 4] that supported the rt-plasma mechanism.

Significant Balmer α line broadening corresponding to an average hydrogen atom temperature of 14 eV and 24 eV was observed for strontium and argon-strontium rt-plasmas and $23\text{-}45 \text{ eV}$ for discharges of strontium-hydrogen, helium-hydrogen, argon-hydrogen, strontium-helium-hydrogen, and strontium-argon-hydrogen, compared to $\approx 3 \text{ eV}$ for pure hydrogen, krypton-hydrogen, xenon-hydrogen, and magnesium-hydrogen. To achieve that same optically measured light output power, sodium-hydrogen, magnesium-hydrogen, and barium-hydrogen mixtures required 4000, 7000, and 6500 times the power of the strontium-

hydrogen mixture, respectively, and the addition of argon increased these ratios by a factor of about two. A glow discharge plasma formed for strontium-hydrogen mixtures at an extremely low voltage of about 2 V compared to 250 V for hydrogen alone and sodium-hydrogen mixtures, and 140-150 V for magnesium-hydrogen and barium-hydrogen mixtures [1-2, 4]. These voltages are too low to be explicable by conventional mechanisms involving accelerated ions with a high applied field.

To further characterize argon-strontium rt-plasmas, plasma formation was studied relative to mixtures of hydrogen and a chemically similar control that does not have electron ionization energies which are a multiple of 27.2 eV , and the Balmer lines were recorded by visible spectroscopy to confirm that an energetic hydrogen plasma was present having H energy states greater than 12 eV corresponding to $n \geq 3$ in Eqs. (1-2). The broadening of the Balmer α line was also recorded as a function of time, and thermal power balance measurements were performed. The cell comprised a titanium or tungsten filament to heat and vaporize some strontium as a source of catalyst and to dissociate molecular hydrogen to atomic hydrogen. The addition of argon to the plasma further provided the catalyst Ar^+ .

Since a conventional discharge power source was not present, the formation of a plasma would require an energetic reaction. The origin of Doppler broadening is the relative thermal motion of the emitter with respect to the observer—in this case the spectrometer. Line broadening is a measure of the atom temperature, and a significant increase was expected and observed for catalysts from strontium or argon with hydrogen. The observation of a high hydrogen temperature with no conventional explanation would indicate that an rt-plasma must have a source of free energy. An energetic chemical reaction was further indicated since it was found that the broadening is time dependent. Therefore, the thermal power balance was measured calorimetrically. To maintain a constant level of ionized argon and strontium as catalysts, a DC glow discharge of plasma of argon-hydrogen (97/3%)-strontium was maintained using a hollow anode. The energy balance was measured by water bath calorimetry. We report the results of these characterizations and discuss the implications regarding the rt-plasma mechanism in Secs. 3A-C.

2. Experimental

Balmer Line Broadening. An argon-hydrogen (97/3%)-strontium rt-plasma was generated in the experimental set up (Figure 1) described previously [1-4] comprising a thermally insulated quartz cell with a cap that incorporated ports for gas inlet, and outlet. A titanium filament (55 cm long, 0.5 mm diameter) that served as a heater and hydrogen dissociator was in the quartz tube. 2.5 g of magnesium or strontium metal (Alfa Aesar 99.95%) was placed in the center of the cell under one atmosphere of dry argon in a glovebox.

The cell was sealed and removed from the glovebox. The cell was maintained at 50 °C for four hours with helium flowing at 30 sccm at a pressure of 0.6 Torr. The filament power was increased to 120 W in 20 increments every 20 minutes. At 120 W, the filament temperature was estimated to be in the range 800 to 1000 °C. The external cell wall temperature was about 700 °C. The cell was then operated with and without an argon-hydrogen (90/10%) flow rate of 5.5 sccm maintained at 0.6 Torr. Additionally, the cell was operated with hydrogen and argon-hydrogen (90/10%) gas flow and no metal. Each metal was vaporized by the filament heater. The presence of a hydrogen plasma was determined by recording the visible spectrum over the Balmer region with a Jobin Yvon Horiba 1250 M spectrometer with a PMT detector described previously [8-9] using entrance/exits slits of 200/100 μm , 0.1 Å step size, and a 3 s integration time. The width of the 656.3 nm Balmer α line emitted from the argon-hydrogen (90/10%)-strontium rt-plasma having a titanium filament was measured initially and periodically during operation. The Balmer profile was also recorded on the air-gap, glow discharge reactor described in the next section with an input power of 20 W ($V=200$; $I=0.1\text{A}$).

Power balance measurements. The power balance of a rt-plasma of strontium with argon-hydrogen mixture (95/5%) maintained in an air-gap, glow discharge reactor shown in Figure 2 was measured by water bath calorimetry using the experimental setup shown in Figure 3. Excess power was observed from argon-hydrogen-strontium plasmas compared to calibration control experiments with the same input power.

The reaction cell comprised a cylindrical stainless steel case of 5.1 cm OD and 17.2 cm in length welded to a set of high vacuum, 8.6 cm diameter Con-flat flanges, as shown in Figure 2. A silver plated copper gasket was placed between a mating flange and the cell flange. The two flanges were clamped together with 10 circumferential bolts. The top-mating flange had a radial centered stainless steel hollow feed through that extended 8.6 cm into the cell and was partially covered by a 3.6 cm long ceramic sleeve, measured from the flange. Gas was fed into the cell by a 1 cm OD stainless steel tube welded to the top-mating flange. Gas flow was controlled by a 0-20 sccm range mass flow controller (MKS model M100B21CS1BV). The cell pressure was monitored by a 0-10 Torr MKS Baratron (model 626A11TEE) absolute pressure gauge. Additionally, the top-mating flange had a drilled thermo well that housed a stainless steel thermocouple (0.3 cm OD). Two 1 cm OD stainless steel tubes were welded to the bottom wall of the reaction cell. One carried the exhaust gas, and the other served as a connection port for a 0.6 cm OD and 16.5 cm long quartz rod to perform optical emission spectroscopy studies. In an oxygen free environment (glove box), 4 grams of strontium distributed in 15 pieces was loaded into the reaction cell and placed below the hollow electrode

as shown in Figure 2, the reaction cell was transferred into the stainless steel jacket, and all the gas and electrical connections were fitted and checked for leaks.

The reaction cell was housed inside a cylindrical stainless steel jacket of 15.2 cm OD and 30.5 cm in length with a removable front flange having welded Ultratorr connectors that fit the reaction cell gas line and the thermocouple. The bottom wall of the stainless steel jacket had two welded Ultratorr connections that fitted the reaction cell exhaust gas and the quartz rod connection port. Two 0.41 cm OD copper power feed-throughs were welded on the side wall and that provided electrical connectors for the reaction cell when it was placed inside the stainless steel jacket. The jacket housing containing the reaction cell was placed inside the drained water bath container, the gas inlet and outlet tubes were connected to the gas/vacuum manifold, as shown in Figure 3.

The water bath (Figure 3) comprised an insulated reservoir filled with 41 liters of de-ionized water. The water was agitated with a paddle driven by a stirring motor. A high precision linear response thermistor probe (Omega OL-703) recorded the temperature of the water bath as a function of time for the stirrer alone to establish the baseline. The water bath was calibrated by a high precision heater (Watlow LGEX17B Type CR-I, with a Xantrex XDC power supply $0-6000 \pm 0.01$ W). Each experiment comprised three distinctive periods: pre-period, heating period, and post period. The pre-period was performed with no power applied to the electrode or to the heater during the reaction test or calibration test, respectively. During the heating period, power was applied through the electrode or through the heater. In the post period, the power applied during the heating period was turned off. The water of the bath was agitated with a stirrer spinning at constant speed throughout all three periods.

The heat capacity was determined for several input powers, 10, 20, 30, 40, and 50 W ± 0.01 W, and was found to be independent of input power over this power range within ± 1.8 %. The temperature rise of the reservoir as a function of time gave a slope in $^{\circ}\text{C/s}$. This slope was baseline corrected for the stirrer power and loss to ambient. The constant known input power (J/s), was divided by this slope to give the heat capacity in J/ $^{\circ}\text{C}$. Then, in general, the total power output from the cell to the reservoir was determined by multiplying the heat capacity by the rate of temperature rise ($^{\circ}\text{C/s}$) to give J/s.

The power balance for a plasma system consisting of the contents of the water bath calorimeter is [23]

$$\dot{H} = \dot{M}(\hat{H}_{in} - \hat{H}_{out}) + \dot{Q}_{plasma} + \dot{Q}_{power\ cable} + \dot{Q}_{stirrer} + \dot{Q}_{heat\ exchange} \quad (4)$$

where H's are enthalpy values (inlet and outlet gases as indicated by the subscripts in and out, respectively, and the hat designates per mole), \dot{M} is the molar flow rate, and the \dot{Q} 's are heat flow rates. It is clear from Eq. (4) that a correction must be considered both for the gas flow term (first term, right side), ' $\dot{Q}_{power\ cable}$ ' which represents the input of the section (approx. 80 cm long) of the power cable that passes through the water bath as it brings power to the discharge, for the work of the stirrer, and for the heat exchange between the insulated water bath and its surroundings.

The values of ' $\dot{Q}_{power\ cable}$ ' and the heat carried out with the gas were small, as determined by appropriate temperature readings. Thermocouples were employed to measure the temperature of the input and output gas, as well as the temperature of the power cable just outside the water bath. Given that the temperature of the power cable was the same as the water bath, $\dot{Q}_{power\ cable}$ was taken as zero. The gas temperature change between input to the plasma and output from the water bath was never more than 1 K. Heat transfer from cell containing the flowing gas to the water in the bath was clearly very efficient. Given the flow rate was 1 sccm, this requires a maximum correction of less than 10^{-6} W, a trivial correction. The stirrer and heat exchange terms were found to be the most significant correction, but its value was readily determined by measuring the temperature rise with only the stirrer operating. This correction can be accurately calculated from the slope of the pre- and post-heating periods and was found to be constant, 5.0 W for all experiments. Once these relatively trivial corrections are made, the 'effective' energy balance becomes:

$$\dot{H} = \dot{Q}_{plasma} \quad (5)$$

The calibration procedure resulted in a linear change in temperature for constant power inputs. This is expected, given the nearly constant heat capacity of water over small changes in temperature (<14 K in all cases). Thus, changes in enthalpy can be readily equated with change in temperature of the bath. In short:

$$\dot{H} = C_p \dot{T} = \dot{Q}_{plasma} \quad (6)$$

Thus, one must only multiply the calibration constant by the rate of change of bath temperature to obtain the plasma's heating power of the water bath. In the event that the change in temperature is nearly linear with time, as it was in all cases in this study, the rate (W) of heat input from the plasma to the bath can be readily determined, and compared with the input power. The rt-plasma results were compared with the results of the calibration control experiment determined using the same analytical procedure.

Since the cell and water bath system were adiabatic, the general form of the power balance equation with the possibility of excess power is:

$$P_{in} + P_{ex} - P_{out} = 0 \quad (7)$$

where P_{in} is the input discharge or heater power, P_{ex} is the excess power generated from the hydrogen catalysis reaction, and P_{out} is the thermal power loss from the cell to the water bath.

The plasma voltage and current reached steady state in about 5 to 10 minutes after the heating period started, and the temperature measured at the wall of the cell typically reached a steady state in about 1 to 2 hrs after the heating period was started. At this point, the power lost from the cell P_{out} was equal to the power supplied to the cell, P_{in} , plus any excess power P_{ex} .

$$P_{in} + P_{ex} = P_{out} \quad (8)$$

Since the cell was surrounded by water that was contained in an insulated reservoir with negligible thermal losses as discussed above, the temperature response of the thermistor T as a function of time t was modeled by a linear curve

$$\dot{T}(t) = a^{-1} P_{out} \quad (9)$$

where a is the heat capacity (J/°C) for the least square curve fit of the response to power input for the control experiments ($P_{ex} = 0$). The slope was recorded for about 25 hours after the cell was started, to achieve an accuracy of $\pm 1.8\%$.

The slope of the temperature rise as a function of time was recorded for each run and baseline corrected for the stirrer power and loss to ambient, then the output power was calculated from the corrected slope. After the calorimeter was calibrated, $\dot{T}(t)$ was recorded with a selected power to the plasma and compared to the results of identical input to the heater in a separate run of the identical system. The higher slope produced with argon-hydrogen-strontium plasma, having Sr^+ and Ar^+ as catalysts and atomic hydrogen as a reactant, compared with controls with no hydrogen and no catalyst present was representative of the excess power. In the case of the catalysis run, the total output power P_{out} was determined by solving Eq. (9) using the measured $\dot{T}(t)$ and the heat capacity a . The excess power P_{ex} was determined from Eq. (8).

3. Results and discussion

A. RT-plasma emission

An argon-hydrogen (90/10%)-strontium rt-plasma formed with a low field (1 V/cm), at low temperatures (e.g. $\approx 10^3$ K), from atomic hydrogen generated at a titanium filament and strontium which was vaporized by heating the metal. H Balmer emission corresponding to population of a level with energy >12 eV was observed as shown in Figure 4 which also requires that Lyman emission was present. No plasmas formed when magnesium replaced strontium or with hydrogen, argon/hydrogen, or strontium alone. This result indicates that the

emission was due to a reaction of hydrogen with vaporized strontium. No possible chemical reactions of the titanium filament, the vaporized strontium, and 0.6 Torr argon-hydrogen mixture at a cell temperature of 700°C could be found, which accounted for the Balmer emission. In fact, no known chemical reaction releases enough energy to excite Balmer and Lyman emission from hydrogen. In addition to known chemical reactions, electron collisional excitation, resonant photon transfer, and the lowering of the ionization and excitation energies by the state of "non ideality" in dense plasmas were also rejected as the source of ionization or excitation to form the hydrogen plasma [15]. The formation of an energetic reaction of atomic hydrogen was consistent with a source of free energy from the catalysis of atomic hydrogen by Sr^+ and Ar^+ .

B. Balmer α line widths

The energetic hydrogen atom energies were calculated from the Doppler width of the 656.3 nm Balmer α line emitted from RF rt-plasmas [8-9]. The full half-width $\Delta\lambda_t$ of each Gaussian results from the Doppler ($\Delta\lambda_D$) and instrumental ($\Delta\lambda_i$) half-widths:

$$\Delta\lambda_t = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_i^2} \quad (10)$$

$\Delta\lambda_i$ in our experiments was 0.006 nm. The temperature was calculated from the Doppler half-width using the formula:

$$\Delta\lambda_D = 7.16 \times 10^{-7} \lambda_0 \left(\frac{T}{\mu} \right)^{1/2} \quad (11)$$

where λ_0 is the line wavelength, T is the temperature in K ($1 \text{ eV} = 11,605 \text{ K}$), and μ is the molecular weight (=1 for atomic hydrogen). In each case, the average Doppler half-width that was not appreciably changed with pressure varied by $\pm 5\%$ corresponding to an error in the energy of $\pm 10\%$.

The 656.3 nm Balmer α line widths recorded on the argon-hydrogen (90/10%)-strontium rt-plasma having a titanium filament initially and after 70 hours of operation are shown in Figure 4. Significant broadening was not observed initially. However, the Balmer α line profile of the plasma emission after 70 hours comprised two distinct Gaussian peaks, an inner, narrower peak corresponding to a slow component with an average hydrogen energy of 1 eV and an outer broader peak corresponding to a fast component of 20 eV. Only the hydrogen lines were broadened. These results are consistent with the catalysis of hydrogen to lower-states followed by subsequent transitions with increasing energy release by an autocatalytic mechanism previously reported with spectroscopic evidence [7-8].

We have assumed that Doppler broadening due to thermal motion was the dominant source to the extent that other sources may be neglected. This assumption was confirmed

when each source was considered. In general, the experimental profile is a convolution of two Doppler profiles, an instrumental profile, the natural (lifetime) profile, Stark profiles, van der Waals profiles, a resonance profile, and fine structure. The contribution from each source was determined to be below the limit of detection [1-6, 8-14, 16, 19-20, 23].

The emission spectrum from the hollow anode, glow discharge of argon-hydrogen (95/5%)-strontium (Figure 5a) showed an intense Sr^+ (407.77 nm) line. The selectively Doppler-broadened 656.3 nm Balmer α line width recorded with a high resolution visible spectrometer corresponding to an average hydrogen hot atom temperature of 50.2 eV with a 83.5% population is shown in Figures 5b and 5c. The independence of the broadening and the peak shape with position in the cell or the dependence on applied voltage or pressure over a broad range excludes the only conventional explanation of a field acceleration mechanism as discussed previously [1-6, 8-14, 16, 19-20, 23].

The formation of fast H can be explained by a resonant energy transfer from hydrogen atoms to Sr^+ or Ar^+ ions of two and one times the potential energy of atomic hydrogen, respectively, followed by a collisional energy transfer to yield fast $H(n=1)$, as well as the emission of $q \cdot 13.6$ eV photons reported previously [5-7]. For example, the exothermic chemical reaction of $H + H$ to form H_2 does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M , to remove the bond energy- $H + H + M \rightarrow H_2 + M^*$ [30]. The third body distributes the energy from the exothermic reaction, and the end result is the H_2 molecule and an increase in the temperature of the system. In the case of the catalytic reaction with the formation of states given by Eqs. (1) and (3), the temperature of H becomes very high.

C. Power balance of the rt-plasma cell

The thermogram, $T(t)$ response of the air-gap reactor with an input power of 10 W to maintain an argon-hydrogen (95/5%)- Sr^+ plasma compared to the heater calibration with stirring only and with a constant input power to the high precision heater of 10 W is shown in Figure 6a. It is evident that the value of the heating slope of the calibration experiment (heater) is smaller than the value of the reaction test, implying that for the same experimental conditions and input power, the rt- plasma transferred more heat to the water than the control performed using the high precision heater. According to Eq. (6), the water bath temperature is a direct indication of the amount of heat generated inside the reaction cell and transferred to the system; therefore, the results of this study show that the argon-hydrogen (95/5%)-strontium plasma generated heat in excess of the input power.

The average baseline corrected least squares fit of the slope, $\dot{T}(t)$, for several calibrations was $5.23 \times 10^{-5} \text{ }^\circ\text{C/s}$, and the heat capacity determined from Eqs. (8-9) with $P_{ex} = 0$, and $P_m = P_{out} = 10 \text{ W}$ was $1.911 \times 10^5 \text{ J/}^\circ\text{C}$. Then the temperature response of the calorimeter for any case (Eq. (9)) was determined to be

$$\dot{T}(t) = (1.911 \times 10^5 \text{ J/}^\circ\text{C})^{-1} \times P_{out} \quad (12)$$

Also a plot of the evolution of excess heat as a function of time can be obtained by using the same heat capacity multiplied by the delta temperature between the reaction and calibration test profiles and further dividing by the time increment:

$$P_{ex}^i = \frac{C_p(T_r^i - T_c^i)}{t_i - t_0} \quad (13)$$

where P_{ex}^i is the excess heat, T_r^i and T_c^i are the water bath temperature of the reaction test and the calibration test at time t_i , respectively, and t_0 is the time at which the heating period started. The excess power obtained for the plasma reaction as a function of time determined by using the measured $\dot{T}(t)$, the input power of 10.0 W, and Eqs. (8) and (9), is shown in Figure 6b. The typical excess heat observed was 2.85 W. These results agree with those obtained using Eq. (13). Sources of error were the error in the calibration curve ($\pm 0.05 \text{ W}$) and the measured input power ($\pm 0.01 \text{ W}$). The propagated error of the calibration and power measurements was $\pm 0.05 \text{ W}$.

Given an argon-hydrogen (95/5%) flow rate of 1.0 sccm and an average excess power of 2.85 W, energy balances of over $-7.7 \times 10^4 \text{ kJ/mole } H_2$ (471 eV/H atom) were measured. The reaction of hydrogen to form water, which releases $-241.8 \text{ kJ/mole } H_2$ (1.48 eV/H atom) is about 320 times less than that observed. The results indicate that once an atom given by Eqs. (1) and (3) is formed by a catalyst, further catalytic transitions $n = \frac{1}{3} \rightarrow \frac{1}{4}, \frac{1}{4} \rightarrow \frac{1}{5}$, and so on, occur to a substantial extent. This is consistent with the series of lower-energy hydrogen lines with energies of $q \cdot 13.6 \text{ eV}$ where $q = 1, 2, 3, 4, 6, 7, 8, 9$, or 11 [5-7], the previously given theory [1-7, 27-29], and previous studies which show very large energy balances [6, 10, 14, 22-23]. These results were confirmed by Calvet and water-flow calorimetry.

4. Conclusion

An rt-plasma formed with a low field (1V/cm), at low temperatures (e.g. $\approx 10^3$ K), from argon and atomic hydrogen generated at a titanium filament with strontium which was vaporized by heating the metal. Strong Balmer emission was observed that indicated an energy source of > 12 eV. The energetic reaction of atomic hydrogen was anticipated to form energetic hydrogen atoms. Significant Balmer α line broadening corresponding to an average hydrogen atom temperature of 20 eV was observed. The time-dependence of the appearance of fast H supported an energetic chemical reaction as the source. The power balance of a rt-plasma with Sr^+ and Ar^+ as catalysts was measured by water bath calorimetry. An average excess power of 2.85 W was observed. The enthalpy of formation ΔH_f of strontium hydride is -199.1 kJ/mole (1.0 eV/H atom) [32]. Thus, the energy for hydriding all of the 4 g (46 mmoles) of strontium would be 9.2 kJ compared to the energy released over the 25 hours of reaction time of 257 kJ. Thus, an excess power of 2.85 W measured calorimetrically on rt-plasmas with Sr^+ and Ar^+ as catalysts and atomic hydrogen as a reactant, compared with controls with no hydrogen and no catalyst present was representative of the excess power. This observation supported the rt-plasmas mechanism since there is no known chemistry which could account for the observed power.

Acknowledgments

Special thanks to M. Nansteel for the calorimetric design and analysis.

References

1. R. Mills and M. Nansteel, P. Ray, "Argon-Hydrogen-Strontium Discharge Light Source", IEEE Transactions on Plasma Science, Vol. 30, No. 2, (2002), pp. 639-653.
2. R. Mills, M. Nansteel, and P. Ray, "Excessively Bright Hydrogen-Strontium Plasma Light Source Due to Energy Resonance of Strontium with Hydrogen", J. of Plasma Physics, Vol. 69, (2003), pp. 131-158.
3. R. Mills, J. Dong, Y. Lu, "Observation of Extreme Ultraviolet Hydrogen Emission from Incandescently Heated Hydrogen Gas with Certain Catalysts", Int. J. Hydrogen Energy, Vol. 25, (2000), pp. 919-943.
4. R. Mills and M. Nansteel, P. Ray, "Bright Hydrogen-Light Source due to a Resonant Energy Transfer with Strontium and Argon Ions", New Journal of Physics, Vol. 4, (2002), pp. 70.1-70.28.
5. R. L. Mills, P. Ray, "Extreme Ultraviolet Spectroscopy of Helium-Hydrogen Plasma", J. Phys. D, Applied Physics, Vol. 36, (2003), pp. 1535-1542.

6. R. L. Mills, P. Ray, B. Dhandapani, M. Nansteel, X. Chen, J. He, "New Power Source from Fractional Quantum Energy Levels of Atomic Hydrogen that Surpasses Internal Combustion", *J Mol. Struct.*, Vol. 643, No. 1-3, (2002), pp. 43-54.
7. R. Mills, P. Ray, "Spectral Emission of Fractional Quantum Energy Levels of Atomic Hydrogen from a Helium-Hydrogen Plasma and the Implications for Dark Matter", *Int. J. Hydrogen Energy*, Vol. 27, No. 3, (2002), pp. 301-322.
8. R. L. Mills, P. Ray, B. Dhandapani, R. M. Mayo, J. He, "Comparison of Excessive Balmer α Line Broadening of Glow Discharge and Microwave Hydrogen Plasmas with Certain Catalysts", *J. of Applied Physics*, Vol. 92, No. 12, (2002), pp. 7008-7022.
9. R. L. Mills, P. Ray, B. Dhandapani, J. He, "Comparison of Excessive Balmer α Line Broadening of Inductively and Capacitively Coupled RF, Microwave, and Glow Discharge Hydrogen Plasmas with Certain Catalysts", *IEEE Transactions on Plasma Science*, Vol. 31, No. (2003), pp. 338-355.
10. R. L. Mills, P. Ray, "Substantial Changes in the Characteristics of a Microwave Plasma Due to Combining Argon and Hydrogen", *New Journal of Physics*, www.njp.org, Vol. 4, (2002), pp. 22.1-22.17.
11. R. Mills, K. Akhtar, B. Dhandapani, "Tests of Features of Field-Acceleration Models for the Extraordinary Selective H Balmer α Broadening in Certain Hydrogen Mixed Plasmas", submitted.
12. J. Phillips, C. Chen, "Evidence of Energetic Reaction Between Helium and Hydrogen Species in RF Generated Plasmas", submitted.
13. J. Phillips, C-K Chen, K. Akhtar, B. Dhandapani, R. Mills, "Evidence of Catalytic Production of Hot Hydrogen in RF Generated Hydrogen/Argon Plasmas", submitted.
14. R. Mills, P. Ray, B. Dhandapani, W. Good, P. Jansson, M. Nansteel, J. He, A. Voigt, "Spectroscopic and NMR Identification of Novel Hydride Ions in Fractional Quantum Energy States Formed by an Exothermic Reaction of Atomic Hydrogen with Certain Catalysts", *European Physical Journal-Applied Physics*, Vol. 28, (2004), pp. 83-104.
15. H. Conrads, R. Mills, Th. Wrubel, "Emission in the Deep Vacuum Ultraviolet from a Plasma Formed by Incandescently Heating Hydrogen Gas with Trace Amounts of Potassium Carbonate", *Plasma Sources Science and Technology*, Vol. 12, (2003), pp. 389-395.
16. R. L. Mills, P. Ray, "A Comprehensive Study of Spectra of the Bound-Free Hyperfine Levels of Novel Hydride Ion $H^- (1/2)$, Hydrogen, Nitrogen, and Air", *Int. J. Hydrogen Energy*, Vol. 28, No. 8, (2003), pp. 825-871.

17. R. Mills, P. Ray, "Spectroscopic Identification of a Novel Catalytic Reaction of Potassium and Atomic Hydrogen and the Hydride Ion Product", *Int. J. Hydrogen Energy*, Vol. 27, No. 2, (2002), pp. 183-192.
18. R. Mills, "Spectroscopic Identification of a Novel Catalytic Reaction of Atomic Hydrogen and the Hydride Ion Product", *Int. J. Hydrogen Energy*, Vol. 26, No. 10, (2001), pp. 1041-1058.
19. R. Mills, P. Ray, R. M. Mayo, "CW HI Laser Based on a Stationary Inverted Lyman Population Formed from Incandescently Heated Hydrogen Gas with Certain Group I Catalysts", *IEEE Transactions on Plasma Science*, Vol. 31, No. 2, (2003), pp. 236-247.
20. R. L. Mills, P. Ray, "Stationary Inverted Lyman Population Formed from Incandescently Heated Hydrogen Gas with Certain Catalysts", *J. Phys. D, Applied Physics*, Vol. 36, (2003), pp. 1504-1509.
21. R. Mills, P. Ray, R. M. Mayo, "The Potential for a Hydrogen Water-Plasma Laser", *Applied Physics Letters*, Vol. 82, No. 11, (2003), pp. 1679-1681.
22. J. Phillips, R. L. Mills, X. Chen, "Water Bath Calorimetric Study of Excess Heat in 'Resonance Transfer' Plasmas", *Journal of Applied Physics*, Vol. 96, No. 6, pp. 3095-3102.
23. R. L. Mills, X. Chen, P. Ray, J. He, B. Dhandapani, "Plasma Power Source Based on a Catalytic Reaction of Atomic Hydrogen Measured by Water Bath Calorimetry", *Thermochimica Acta*, Vol. 406/1-2, (2003), pp. 35-53.
24. R. Mills, B. Dhandapani, M. Nansteel, J. He, T. Shannon, A. Echezuria, "Synthesis and Characterization of Novel Hydride Compounds", *Int. J. of Hydrogen Energy*, Vol. 26, No. 4, (2001), pp. 339-367.
25. R. Mills, B. Dhandapani, N. Greenig, J. He, "Synthesis and Characterization of Potassium Iodo Hydride", *Int. J. of Hydrogen Energy*, Vol. 25, Issue 12, December, (2000), pp. 1185-1203.
26. R. Mills, B. Dhandapani, M. Nansteel, J. He, A. Voigt, "Identification of Compounds Containing Novel Hydride Ions by Nuclear Magnetic Resonance Spectroscopy", *Int. J. Hydrogen Energy*, Vol. 26, No. 9, (2001), pp. 965-979.
27. R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, May (2006) Edition posted at www.blacklightpower.com.
28. R. L. Mills, "The Nature of the Chemical Bond Revisited and an Alternative Maxwellian Approach", *Physics Essays*, Vol. 17, No. 3, (2004), pp. 342-389.
29. R. L. Mills, "Exact Classical Quantum Mechanical Solutions for One- Through Twenty-Electron Atoms", in press.
30. N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Volume I, Oxford, Clarendon Press, (1950), p.17.

31. M. D. Lamb, *Luminescence Spectroscopy*, Academic Press, London, (1978), p. 68.
32. W. M. Muller, J. P. Blackledge, G. G. Libowitz, *Metal Hydrides*, Academic Press, New York, (1968), p 201.

Figure Captions

Figure 1. The experimental setup for generating an argon-hydrogen-strontium rt-plasma.

Figure 2. Air-gap reactor comprising a hollow anode DC glow discharge cell and a stainless steel jacket for maintaining an argon-hydrogen (95/5%)- Sr^+ plasma.

Figure 3. Water bath calorimetric system for measuring the power balance on an argon-hydrogen (95/5%)- Sr^+ plasma.

Figure 4. The 656.3 nm Balmer α line width recorded with a high-resolution visible spectrometer on the initial emission of a hydrogen-strontium rt-plasma and the emission at 70 hours of operation. Significant broadening was observed over time corresponding to an average hydrogen atom temperature of 20 eV.

Figure 5. (a) The emission spectrum from a hollow anode, glow discharge of argon-hydrogen (95/5%)-strontium showing an intense Sr^+ (407.77 nm) line. (b) The high resolution spectrum (653.0-659.0 nm) of the argon-hydrogen (95/5%)-strontium plasma emission showing selective broadening of the Balmer α line relative to the argon and strontium atomic lines. (c) The selectively broadened 656.3 nm Balmer α line width recorded with a high-resolution visible spectrometer corresponding to an average hydrogen hot atom temperature of 50.2 eV with a 83.5% population.

Figures 6. (a) Water bath temperature profiles of the air-gap reactor with an input power of 10 W to maintain an argon-hydrogen (95/5%)- Sr^+ plasma compared to the heater calibration. (b) Excess power obtained for the plasma reaction as a function of time.

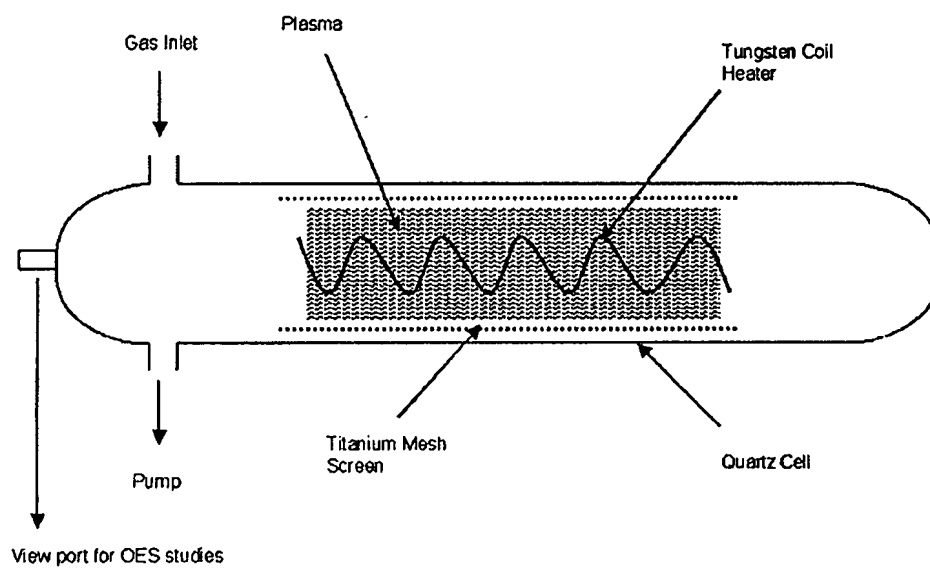


Fig. 1

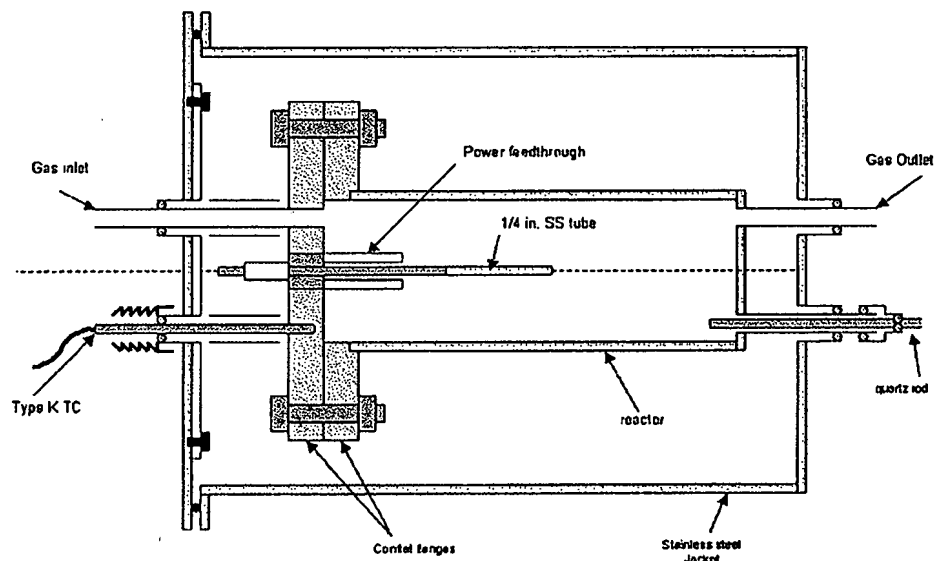


Fig. 2

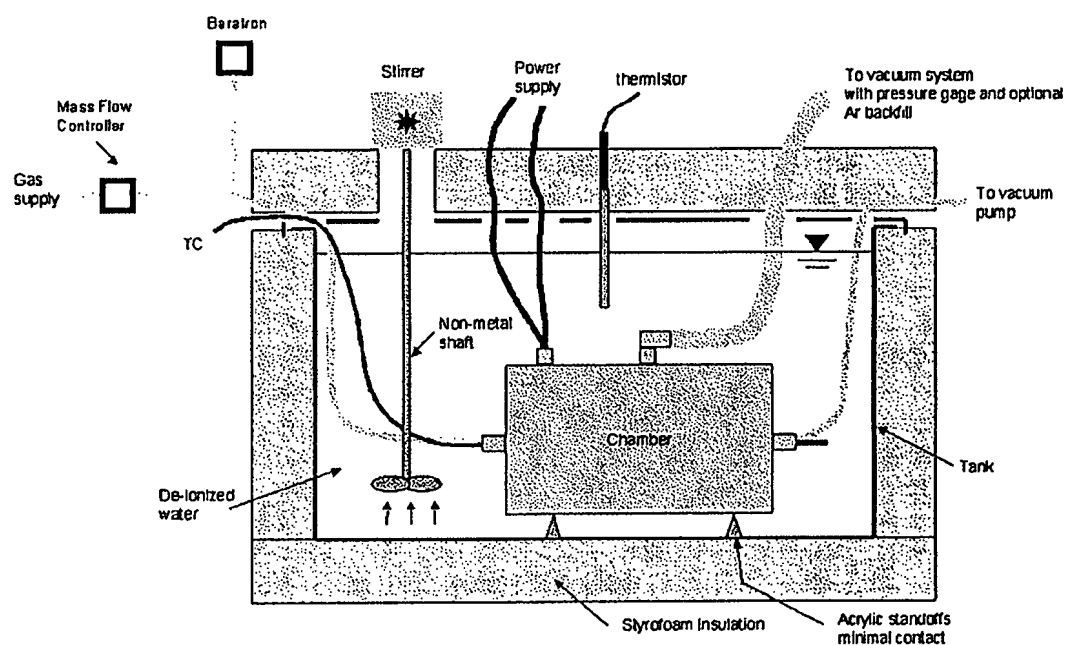


Fig. 3

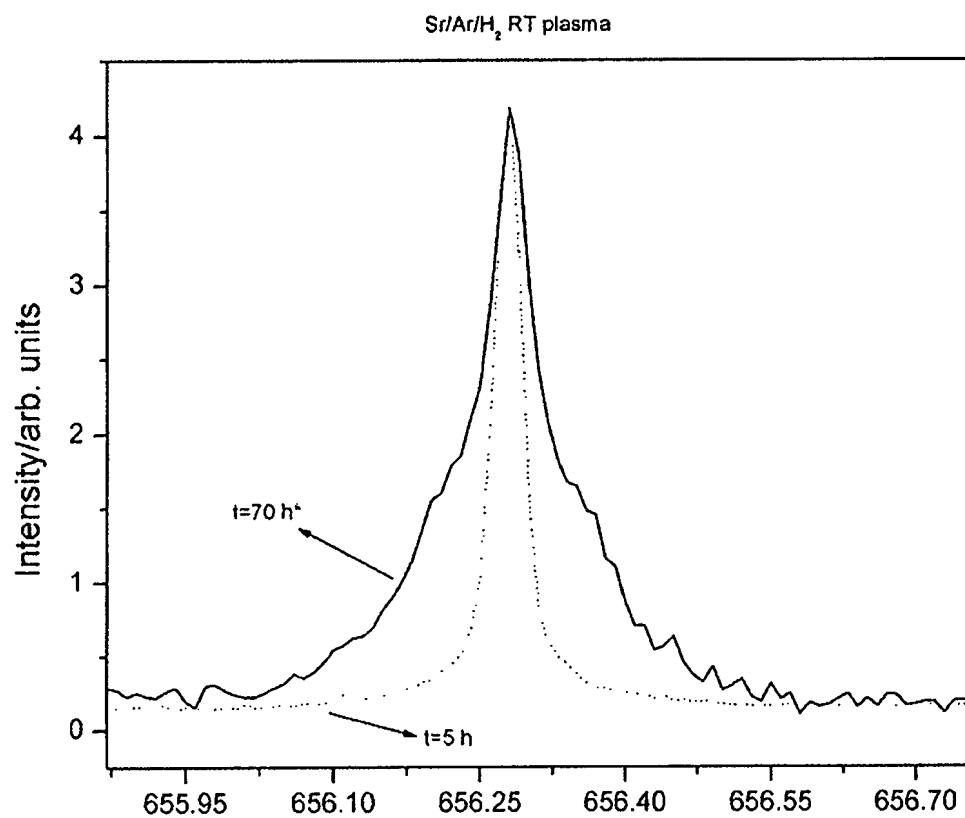


Fig. 4

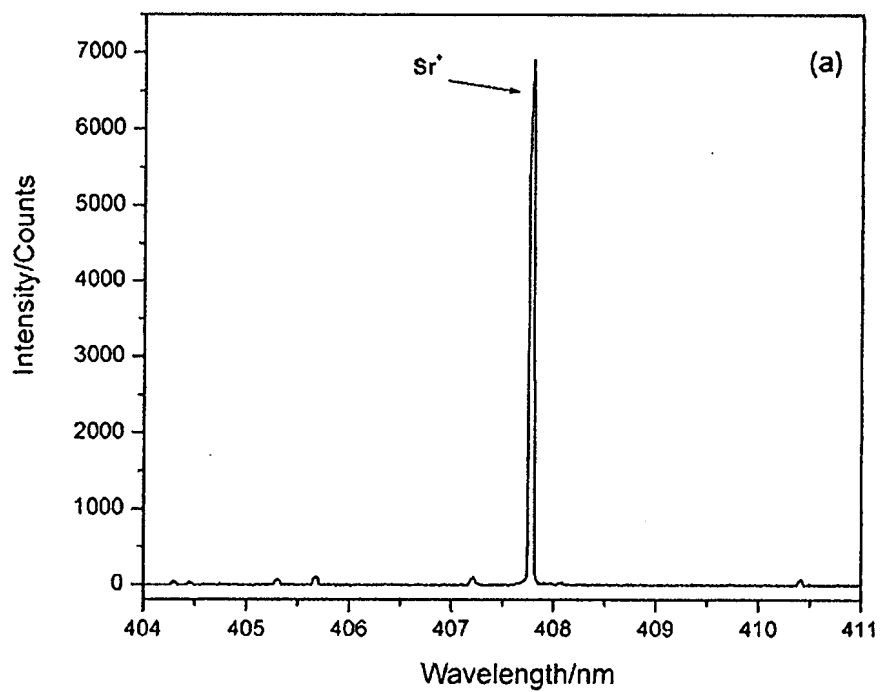


Fig. 5a

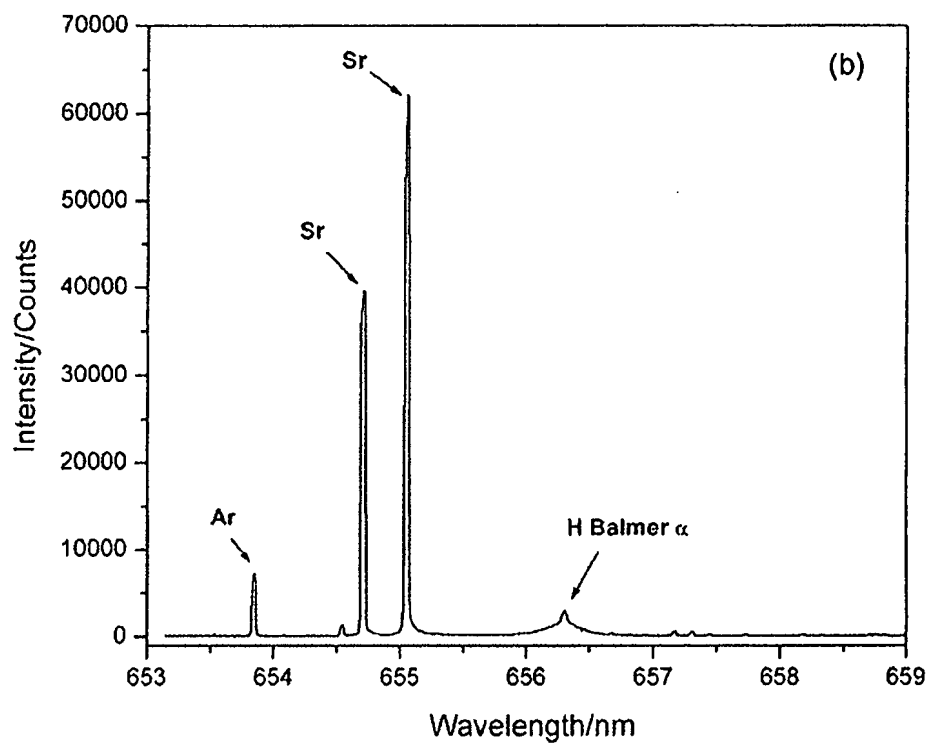


Fig. 5b

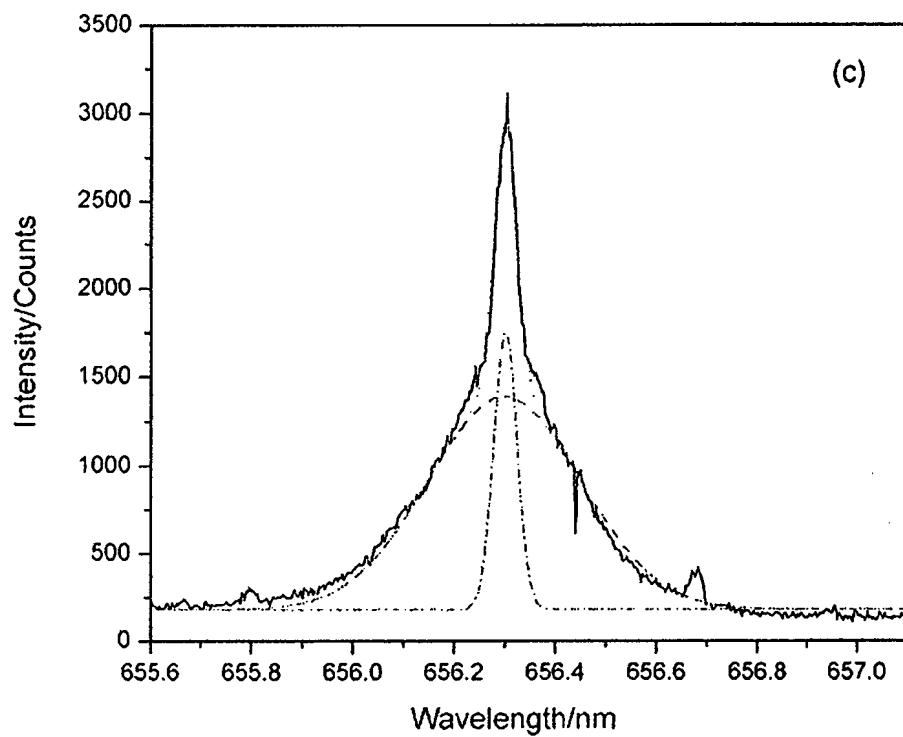


Fig. 5c

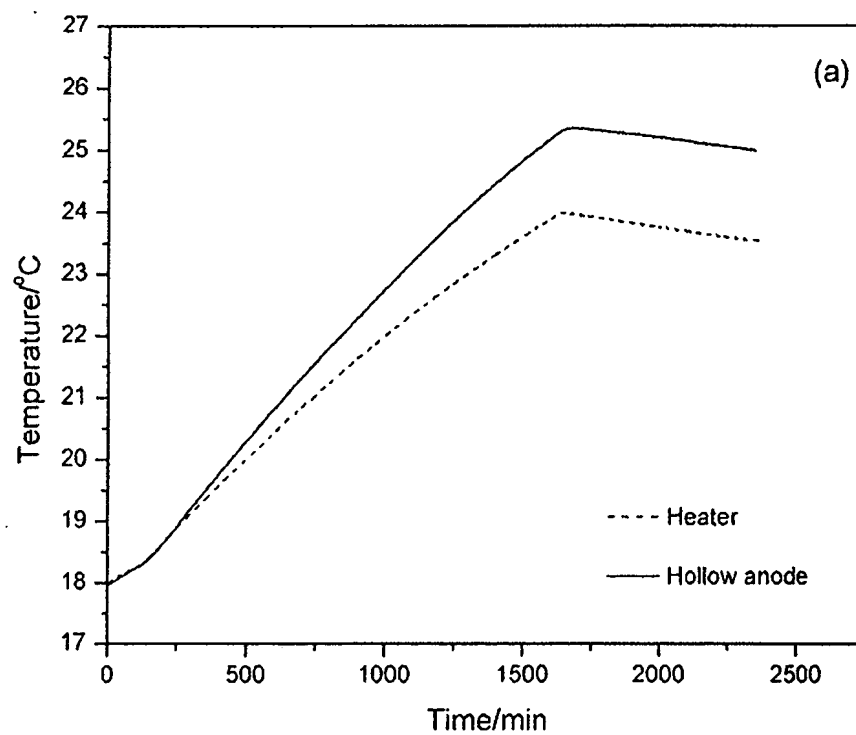


Fig. 6a

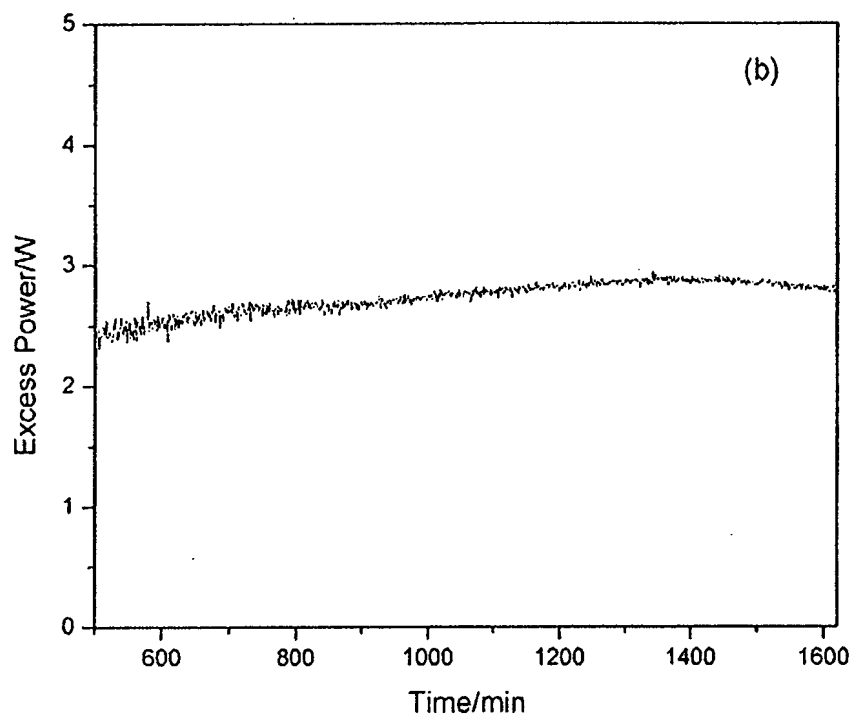


Fig. 6b